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Propulsion Science and Advanced Concepts Division

**In pursuit of the  $\text{PO}_2^+$  cation. The reaction of  $\text{KPO}_2\text{F}_2$  and  $\text{SbF}_5$  leads to an eight-membered, antimony-oxygen-phosphorus-bridged ring<sup>†</sup>**

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*Professor Josef Goubeau in memoriam*

Bei der Redaktion eingegangen am

**Abstract.** The reaction of  $\text{KPO}_2\text{F}_2$  with the strong Lewis acid  $\text{SbF}_5$  was studied as a potential pathway to the unknown  $\text{PO}_2^+$  cation. The resulting product has the desired  $\text{PO}_2\text{SbF}_6$  composition but consists of an eight-membered, oxygen-bridged ring that was

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characterized by vibrational and NMR spectroscopy, *ab initio* methods, and a single crystal x-ray diffraction study. The formation of the oxygen-bridged ring and its mechanism are discussed.

## **Auf der Suche nach dem $\text{PO}_2^+$ Kation. Die Reaktion von $\text{KPO}_2\text{F}_2$ mit $\text{SbF}_5$ führt zu einem achtegliedrigen Sb-O-P verbrückten Ring**

**Inhaltsübersicht.** Auf der Suche nach dem  $\text{PO}_2^+$  Kation wurde die Reaktion von  $\text{KPO}_2\text{F}_2$  mit der starken Lewissäure  $\text{SbF}_5$  untersucht. Das resultierende Produkt mit der gewünschten Zusammensetzung  $\text{PO}_2\text{SbF}_6$  besteht aus einem achtegliedrigen sauerstoffverbrückten Ring der anhand von schwingungs-, NMR-spektroskopischen und *ab initio* Methoden sowie einer Einkristallröntgenstrukturuntersuchung charakterisiert wurde. Der Mechanismus und die Bildung des sauerstoffverbrückten Rings werden diskutiert.

**Keywords:** Phosphoryl cation, eight-membered, P-O-Sb bridged ring, vibrational spectroscopy, NMR spectroscopy, crystal structure, *ab initio* calculations

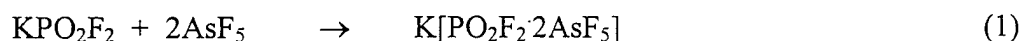
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## Introduction

In view of the long known existence, great stability and general utility of  $\text{CO}_2$ ,  $\text{SiO}_2$  and  $\text{NO}_2^+$ , it is surprising that the closely related  $\text{PO}_2^+$  cation is presently still unknown. The only data available is an *ab initio* calculation on the free gaseous ion [1]. Very little is also known about its parent molecule, phosphoryl fluoride [2,3], however, the corresponding anion,  $\text{PO}_2\text{F}_2^-$ , is well known and characterized [4]. Since anions can generally be converted to the corresponding parent molecules and cations by treatment with a strong Lewis acid, it was interesting to study the reaction of a  $\text{PO}_2\text{F}_2^-$  salt with strong Lewis acids. In a previous study in our laboratory, the interaction between  $\text{KPO}_2\text{F}_2$  and  $\text{AsF}_5$  had been studied [5]. Surprisingly, only an oxygen-bridged polynuclear anion between  $\text{PO}_2\text{F}_2^-$  and two  $\text{AsF}_5$  molecules (eq. (1), Fig. 1) and no  $\text{PO}_2\text{F}$  or  $\text{PO}_2^+$  were observed.



The failure to generate the  $\text{PO}_2^+$  cation in this reaction can be attributed to  $\text{PO}_2\text{F}$  having a Lewis acidity comparable to that of  $\text{AsF}_5$  [6, 7]. Therefore,  $\text{PO}_2\text{F}_2^-$  shares its oxygen ligands with  $\text{AsF}_5$  through the formation of a donor-acceptor adduct rather than give up fluoride ions to form  $\text{PO}_2\text{F}$  or the  $\text{PO}_2^+$  cation. Since  $\text{SbF}_5$  and particularly oligomeric  $\text{SbF}_5$  are much stronger Lewis acids than  $\text{AsF}_5$  [6], it was hoped that the replacement of  $\text{AsF}_5$  in reaction (1) by an excess of  $\text{SbF}_5$  might lead to  $\text{PO}_2^+$ .

Another highly interesting aspect is the most plausible structure of  $\text{PO}_2^+$ . Whereas the minimum energy structure of the free gaseous  $\text{PO}_2^+$  ion is a di-coordinated linear monomer [1] as in  $\text{CO}_2$  and  $\text{NO}_2^+$ , the condensed phase structure of  $\text{PO}_2^+$  is more problematic. Since phosphorus seeks a coordination number higher than two, the  $\text{PO}_2^+$  cations would either have to polymerize, as isoelectronic  $\text{SiO}_2$  does, or undergo fluorine or oxygen bridging with the anions. Of these two choices, the first one is less likely because it would result in an accumulation of mutually repelling positive charges.

## Experimental

### *Materials and Methods*

All volatile materials were handled in either a stainless-steel vacuum line [8] equipped with Teflon-FEP U-traps, 316 stainless-steel bellows-seal valves, and a Heise Bourdon tube-type pressure gauge, or a flamed-out Pyrex glass vacuum line equipped with grease-free Kontes glass Teflon valves. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box.

Infrared spectra were recorded in the range of  $4000\text{--}400\text{ cm}^{-1}$  on a Midac FT-IR Model 1720 at a resolution of  $1\text{ cm}^{-1}$ . Spectra of solids were obtained by using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Spectra of gases were obtained by using a stainless steel cell of 5 cm path length equipped with AgCl windows. Raman spectra were recorded in the range of  $4000\text{--}10\text{ cm}^{-1}$  on a Bruker Equinox 55 FT-RA spectrophotometer using a NdYag laser at  $1064$

nm. Pyrex melting point capillaries or NMR tubes, that were baked out at 300 °C for 48 h at 10 mtorr vacuum, were used as sample containers.

The  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker AM-360 spectrometer equipped with a 8.45556-T cryomagnet. Samples were measured in heat sealed 4mm glass tubes and referenced to  $\text{CFCl}_3$  ( $^{19}\text{F}$ ) and 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) at 20°C with positive shifts being to high frequency of the reference compounds.

Commercially available urea,  $\text{KH}_2\text{PO}_4$  (Aldrich),  $\text{NH}_4\text{HF}_2$  (Riedel-de-Haen) and  $\text{SO}_2$  (Matheson) were used as received.  $\text{SbF}_5$  (Ozark Mahoning) was purified by distillation prior to use. A literature method was used for the preparation of  $\text{KPO}_2\text{F}_2$  [9] and it showed no impurities detectable by vibrational spectroscopy.

Single crystals of  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  were grown by slow sublimation at 90°C. They were mounted on the goniometer head by the oil-drop method using perfluoropolyether (PFPE) oil and precentered Nylon Cryoloops equipped with a magnetic base. The crystal structure was determined at 203 K using a Bruker diffractometer equipped with a CCD detector and a low temperature, LT3, device. The 3-circle platform with a fixed  $\chi$ -axis was controlled by the SMART [10] software package. The unit cell parameters were determined from three runs of data with 30 frames per run using a scan speed of 30-seconds per frame. A complete hemisphere of data was collected using 1271 frames at 30 sec/frame, including 50 frames that were collected at the beginning and end of the data collection to monitor crystal decay. Data were integrated using the SAINT [11] software package, and the raw data was corrected for absorption using the SADABS [12] program. The structure was solved by the Patterson method using the SHELXS-97 [13] program and refined by the least squares method on  $F^2$  using SHELXL-97 [14]. The crystal did not show any significant decomposition during the data collection. The

experimental and refinement parameters, and the atomic coordinates and thermal displacement parameters are listed in Tables 1 and 2, respectively.

### *Computational Methods*

Infrared and Raman spectra for oxygen- and fluorine-bridged  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  complexes were computed by the density-functional approach using the B3LYP functional [15]. The so-called DFT/DZVP all-electron basis set [16,17], supplemented with one  $f$  function with an exponent of 0.3854 taken from the polarization functions of Ahlrichs [18], was used for antimony, and 6-311G(d) basis sets of Pople *et al.* [19] were used for oxygen, phosphorus, and fluorine. Cartesian coordinates taken from crystal structure determinations were used as a starting point for the geometry optimizations. The calculations were carried out on IBM RS/6000 Model 260 workstations using the Gaussian 98 [20] program system.

### *Syntheses of $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$ and $\text{KPO}_2\text{F}_2 \cdot 2\text{SbF}_5$*

In the drybox,  $\text{KPO}_2\text{F}_2$  (6.39 mmol) was placed into a flamed-out Pyrex glass reaction vessel equipped with a grease-free Kontes glass Teflon valve. On the metal vacuum line, a large excess of  $\text{SbF}_5$  (34.23 mmol) and a few ml of  $\text{SO}_2$  were added to the reaction vessel. After keeping the mixture at room temperature for several hours, the  $\text{SO}_2$  and unreacted  $\text{SbF}_5$  were pumped off and pure, crystalline  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  was obtained in high yield by vacuum sublimation at 95 °C. The colorless solid residue consisted of  $\text{KSbF}_6$  that was identified by vibrational spectroscopy and the observed mass balance.



In another experiment, a 1:2 mixture of  $\text{KPO}_2\text{F}_2$  (13.52 mmol) and  $\text{SbF}_5$  (27.2 mmol) was placed into a flamed-out Pyrex glass vessel. After a couple of weeks at room temperature, all the liquid  $\text{SbF}_5$  had reacted with  $\text{KPO}_2\text{F}_2$  resulting in a dry colorless powder. A comparison of the vibrational spectra of the product with those of the  $\text{KPO}_2\text{F}_2 \cdot 2\text{AsF}_5$  polyanion [5] showed, that the product had the composition  $\text{KPO}_2\text{F}_2 \cdot 2\text{SbF}_5$ .

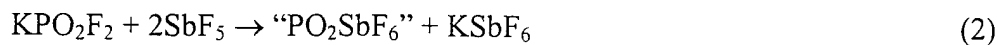
Raman spectral data for  $\text{KPO}_2\text{F}_2 \cdot 2\text{SbF}_5$  (dry powder) [ $\text{cm}^{-1}$  (relative intensity)]: 232(12.8), 294(38.5), 598(2.6), 613(5.1), 659(100), 689(15.4), 956(7.7).

Heating of  $\text{KPO}_2\text{F}_2 \cdot 2\text{SbF}_5$  to 95 °C resulted in the sublimation of  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$ . Further heating of  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  led to slow  $\text{POF}_3$  evolution and produced a colorless liquid of undetermined composition.

## Results and Discussion

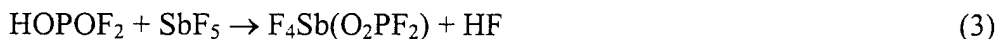
### *Synthesis and Properties of $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$*

The room-temperature reaction of  $\text{KPO}_2\text{F}_2$  with excess  $\text{SbF}_5$  in the presence of a suitable solvent, such as  $\text{SO}_2$ , followed by the removal of the solvent and excess  $\text{SbF}_5$  and a vacuum sublimation at 95 °C, produces  $\text{KSbF}_6$  and a product of the desired composition  $\text{PO}_2\text{SbF}_6$  (eq. 2).



The more volatile "PO<sub>2</sub>SbF<sub>6</sub>" can be readily separated from the KSbF<sub>6</sub> by vacuum sublimation at 95 °C and was obtained in high yield and purity. As will be shown below, this compound does not have a simple PO<sub>2</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup> structure but consists of eight-membered, oxygen-bridged (SbF<sub>4</sub>O<sub>2</sub>PF<sub>2</sub>)<sub>2</sub> units.

A compound with such a structure has been proposed previously by *Krüger, Dehnicke, and Shihada* [21]. It was isolated in 4% yield from the reaction of SbF<sub>5</sub> with HOPOF<sub>2</sub> (eq. 3).



However, its reported properties (fine, white crystals, m.p. 65 °C, decomp.p. 70°C with POF<sub>3</sub> loss) do not agree well with those observed by us for (SbF<sub>4</sub>O<sub>2</sub>PF<sub>2</sub>)<sub>2</sub> (crystalline solid, stable at 95 °C). Also the reported IR spectrum (1230 vs, 1175 s, 1095 w, 1042 s, 961 m, 735 s, 705 vs, etc) shows only fair agreement with our data (see below), but their <sup>31</sup>P NMR spectrum agrees well with that observed in this study. Although in our opinion, *Krüger, Dehnicke and Shihada* had probably prepared the same compound and suggested, by analogy with related known compounds, the correct oxygen-bridged dimeric structure, their compound may have been of poor purity and was not well characterized.

### *Crystal structure of $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$*

The crystals of  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  belong to the centrosymmetric space group P-1. The asymmetric unit cell contains one half of the dimer and the other half is generated by the symmetry operation  $-x+1, -y+2, -z$ . The structure of  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  (Fig. 2, Table 3) shows that the molecule contains an eight-membered  $[\text{Sb-O-P-O}]_2$  ring which adopts a chair conformation where two  $\text{SbF}_4$  units are bridged by two  $-\text{OP}(\text{F}_2)\text{O}-$  groups. The phosphorus and oxygen atoms are coplanar with a maximum mean plane deviation of 0.0186 Å and the antimony atoms are located above and below this plane at 1.1418 Å. There is a significant distortion of the octahedral environment around the antimony atoms due to the two bridging oxygen ligands having considerably longer bonds and, therefore, being less repulsive. The fluorine atoms F1 and F2 are located in a quasi-axial position and are longer by 0.02 Å (average  $\text{Sb-F} = 1.865$  Å) compared to the equatorial fluorine atoms F3 and F4 (average  $\text{Sb-F} = 1.845$  Å). The two  $\text{Sb-O}$  distances are practically identical at 2.004(4) Å and 2.003(4) Å. Due to the presence of the two longer  $\text{Sb-O}$  bonds, the  $\text{F1-Sb1-F2}$  angle is compressed to  $171.2(2)^\circ$  from the ideal value of  $180^\circ$ , the  $\text{O-Sb-O}$  angle is compressed to  $86.4(2)^\circ$ , and the  $\text{F3-Sb1-F4}$  angle is widened to  $93.6(2)^\circ$ . A comparison of the bond distances and angles for  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  with those of closely related  $\text{SbCl}_4$  derivatives [22, 23] is listed in Table 4 and shows good agreement.

The crystal packing diagram of  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  along the  $b$ -axis is shown in Fig. 3. The chair-form molecules make contacts with the neighboring molecules resulting in a polymeric chain. The closest contact distances are  $\text{P1}\cdots\text{F2}$  and  $\text{P1}\cdots\text{F3}$  at 3.295 and 3.277 Å, respectively.

Since oxygen and fluorine atoms are often difficult to distinguish in crystal structures, the possibility of refining our data set for a fluorine-bridged model was also explored. It resulted in a significantly higher R factor and larger thermal parameters of the bridging atoms and was therefore rejected. Further support for the oxygen-bridged model comes from the vibrational spectra and theoretical calculations.

### *Vibrational Spectra and Theoretical Calculations*

The Raman and infrared spectra of  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  are shown in Fig. 4. The observed and calculated vibrational frequencies and IR and Raman intensities are summarized in Table 5. For comparison, the calculated spectra of the fluorine-bridged model have also been listed in this table. As can be seen from Table 5, the observed spectra agree only with the oxygen-bridged but not with the fluorine-bridged model. In a fluorine-bridged structure, the P-O bonds would possess significant double bond character and their antisymmetric stretching vibrations should occur in the  $1500\text{ cm}^{-1}$  region.

The assignments for  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  were made in point group  $C_i$ , in accord with the results from the crystal structure determination and the theoretical calculations which show that  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  possesses only a symmetry center and that no atoms lie on this center. A total of 54 fundamental vibrations are expected out of which one half of them is symmetric ( $A_g$  modes) and the other half is antisymmetric ( $A_u$  modes) to the symmetry center. The  $A_g$  modes are due to the in-phase motions of the symmetry related groups and are only Raman active, while the  $A_u$  modes represent the out-of-phase motions of these groups and are only infrared active. Since the vibrational coupling

between the corresponding  $A_g$  and  $A_u$  modes is relatively weak, their frequency separations are small, except for the four highest frequency modes that are due to the antisymmetric and symmetric in-phase and out-of-phase stretching motions of the  $PO_2$  groups. Therefore, it may appear that some of the bands are active in both the infrared and the Raman spectra, but a closer inspection reveals that their frequencies differ enough to rule out this interpretation. In view of the complexity of the symmetry coordinates for such a large system, a normal coordinate analysis was not carried out for  $(SbF_4O_2PF_2)_2$ .

The total energies, calculated for the oxygen- and the fluorine-bridged structures show that the oxygen-bridged model is favored by  $130 \text{ kcal mol}^{-1}$ . This large energy difference accounts for the preferred formation of the oxygen-bridged rings which can be explained by the following mechanism (Fig. 5).

The first step involves the formation of an oxygen-bridged polynuclear  $[PO_2F_2 \cdot 2SbF_5]^-$  anion, as in the case of  $AsF_5$ . The important difference between  $AsF_5$  and  $SbF_5$  is that antimony can expand its coordination towards fluorine or oxygen past six, while arsenic cannot [24]. This allows the  $SbF_5$  ligand of  $[PO_2F_2 \cdot 2SbF_5]^-$  to interact with a second  $PO_2F_2^-$  anion, as shown in Figure 5. Elimination of two equivalents of  $KF$  then produces the final product. The following experimental evidence supports this mechanism. When a 2:1 molar mixture of  $SbF_5$  and  $KPO_2F_2$  was allowed to interact at room temperature in the absence of a solvent, a colorless powder was obtained that was identified by vibrational spectroscopy as the  $K^+$  salt of the oxygen bridged  $[PO_2F_2 \cdot 2SbF_5]^-$  polyanion. Heating of this salt to  $95^\circ C$  resulted in the sublimation of  $(SbF_4O_2PF_2)_2$  and a  $KSbF_6$  residue (see Experimental Section).

### *NMR Spectra*

A solution of a few single crystals of  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  in  $\text{SO}_2$  was used to record NMR-spectra. The strongest signal in the  $^{31}\text{P}$  spectra was a triplet ( $\delta$  -35.6 ppm,  $^1J_{\text{PF}}$  1030 Hz) that is typical for a  $\text{PO}_2\text{F}_2$  group, but the spectra also exhibited many signals that could not be firmly assigned. The chemical shift and the  $^1J_{\text{PF}}$  coupling constant observed for our triplet agree well with those (t,  $\delta$  -35.5 ppm,  $^1J_{\text{PF}}$  1039 Hz) previously reported by *Dehnicke* et al [21] for an  $\text{SbF}_5$  solution. The  $^{19}\text{F}$  NMR-spectra were even more complicated. Only the signal for the  $\text{PO}_2\text{F}_2$ -group (d,  $\delta$  -80.5 ppm,  $^1J_{\text{PF}}$  1037 Hz) could be assigned. In view of this, it is not certain whether the eight-membered ring persists in  $\text{SO}_2$  solution at room temperature.

### **Conclusion**

The reaction of  $\text{KPO}_2\text{F}_2$  with the strongest presently known Lewis acid, i.e., oligomeric  $\text{SbF}_5$ , does not produce  $\text{PO}_2^+$  salts but oxygen-bridged eight-membered Sb-O-P rings with hexa-coordinated antimony and tetra-coordinated phosphorus. The chances for preparing ionic salts that contain isolated  $\text{PO}_2^+$  cations must be considered very slim because pentavalent phosphorus seeks coordination numbers in excess of two. Since the polymerization of  $\text{PO}_2^+$  is highly unlikely due to the mutual repulsion of charges of the same sign,  $\text{PO}_2^+$  exhibits a strong tendency to undergo oxygen- or fluorine- bridging to

achieve higher coordination. Even the possibility of approximating a  $\text{PO}_2^+$  cation by having a  $\text{PO}_2\text{F}_2^-$  unit forming two fluorine-bridges to very strong Lewis acids is thwarted by energetics. In the eight-membered  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  rings, the oxygen-bridged structure is favored over the fluorine-bridged one by  $130 \text{ kcal mol}^{-1}$ .

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### References

- [1] P. Pyykkö, Y. Zhao, *Mol. Phys.* **1990**, *70*, 701.
- [2] U. Wannagat, J. Rademachers, *Z. Anorg. Allg. Chem.* **1957**, *289*, 66.
- [3] D. W. Muenow, O. M. Uy, J. L. Margrave, *J. Inorg. Nucl. Chem.* **1969**, *31*, 3411.
- [4] A. Addou, P. Vast, P. Legrand, *Spectrochim. Acta, Part A* **1982**, *38A*, 785, and references cited therein.
- [5] K. O. Christe, R. Gnann, R. I. Wagner, W. W. Wilson, *Eur. J. Solid State Inorg Chem.* **1996**, *33*, 865.
- [6] J. W. Larson, T.B. McMahon, *Inorg. Chem.* **1987**, *26*, 4018.

- [7] K. O. Christe, D. A. Dixon, D. McLemore, W.W. Wilson, J. A. Sheehy, J. A. Boatz, *J. Fluorine Chem.* **2000**, *101*, 151.
- [8] K. O. Christe, R. D. Wilson, C. J. Schack, *Inorg. Synth.* **1986**, *24*, 3.
- [9] U. Schuelke, R. Kayser, *Z. Anorg. Allg. Chem.* **1991**, *600*, 221.
- [10] SMART V 4.045 Software for the CCD Detector System, Bruker AXS, Madison, WI 1999.
- [11] SAINT V 4.035 Software for the CCD Detector System, Bruker AXS, Madison, WI 1999.
- [12] SADABS, Program for absorption correction for area detectors, Version 2.01, Bruker AXS, Madison, WI 2000.
- [13] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structure, University of Göttingen, Germany, 1997.
- [14] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997.
- [15] The B3LYP functional uses a three-parameter exchange functional of Becke (B3) [A.D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; P.J. Stephens, C.F. Devlin, C.F. Chabalowski, and M.J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623] and the Lee, Yang, and Parr (LYP) correlation gradient-corrected functional [C. Lee, W. Yang, and R.G. Parr, *Phys. Rev. B* **1988**, *37*, 785].
- [16] These local-spin-density-optimized Gaussian basis sets were developed by Nathalie Godbout and Jan Andzelm, and are made available courtesy of Cray Research, Inc. The general method by which they were developed is given in N.



- Godbout, D.R. Salahub, J. Andzelm, and E. Wimmer, *Can. J. Chem.* **1992**, *70*, 560.
- [17] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version , as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further.
- [18] Polarization functions are unpublished supplements to the basis sets described in A. Schafer, C. Huber, and R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.
- [19] M.J. Frisch, J.A. Pople, and J.S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265.
- [20] Gaussian 98, Revision A.7, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-

- Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, and J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.
- [21] N. Krüger, K. Dehnicke, A. F. Shihada, *Z. Anorg. Allg. Chem.* **1978**, 438, 169.
- [22] A. W. Cooke, J. Pebler, F. Weller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1985**, 524, 68.
- [23] A. F. Shihada, F. Weller, *Z. Anorg. Allg. Chem.* **1981**, 472, 102.
- [24] G. W. Drake, D. A. Dixon, J. A. Sheehy, J. A. Boatz, K. O. Christe, *J. Am. Chem. Soc.* **1998**, 120, 8392.

**Table 1.** Crystal data and structure refinement for (SbF<sub>4</sub>O<sub>2</sub>PF<sub>2</sub>)<sub>2</sub>.

Empirical formula	F <sub>12</sub> O <sub>4</sub> P <sub>2</sub> Sb <sub>2</sub>
Space group	P-1 triclinic
Unit cell dimensions	a = 5.565(4) Å α = 88.685(16)°. b = 7.406(6) Å β = 76.367(16)°. c = 7.443(6) Å γ = 83.364(16)°.
Volume / Å <sup>3</sup>	296.1(4)
ρ <sub>(calculated)</sub> / g cm <sup>-3</sup>	3.350
Z	2
Formula weight	597.44
μ / mm <sup>-1</sup>	5.001
Temperature / K	203(2)
λ (MoKα) / Å	0.71073
Crystal size / mm	0.20 x 0.12 x 0.10
Theta range for data collection θ / °	2.77 to 26.37
Index ranges (hkl)	-6 ≤ h ≤ 6, -9 ≤ k ≤ 9, -9 ≤ l ≤ 9
Reflections collected	2845
Independent reflections	1202 [R(int) = 0.0469]
F(000)	272
Max. and min. transmission	0.565765 and 0.406416
R <sup>a</sup> [I > 2σ(I)]	R1 = 0.0406, wR2 = 0.0987
R <sup>a</sup> (all data)	R1 = 0.0416, wR2 = 0.0997
Largest diff. peak and hole (e Å <sup>-3</sup> )	2.174 and -1.864
Absorption correction	SADABS
Goodness-of-fit on F <sup>2</sup>	1.168
Data / restraints / parameters	1202 / 0 / 91
Refinement method	Full-matrix least-squares on F <sup>2</sup>

(a)  $R = \sum |F_o| - |F_c| / \sum |F_o|$ .

**Table 2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).

	X	Y	z	U(eq) <sup>a</sup>
Sb(1)	4170(1)	7691(1)	2440(1)	20(1)
P(1)	2277(2)	11935(2)	1685(2)	20(1)
F(1)	6657(6)	9178(5)	2470(6)	32(1)
F(2)	1648(6)	6397(5)	2075(5)	29(1)
F(3)	2636(8)	8157(6)	4885(5)	38(1)
F(4)	6091(8)	5603(5)	2912(6)	39(1)
O(2)	4353(8)	12637(6)	276(6)	28(1)
O(1)	2190(7)	9927(5)	1761(6)	26(1)
F(6)	-202(6)	12778(5)	1420(5)	33(1)
F(5)	2419(7)	12638(5)	3522(5)	33(1)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} \mathbf{a}_i^* \mathbf{a}_j^* \mathbf{a}_i \mathbf{a}_j$$

**Table 3.** Bond lengths [ $\text{\AA}$ ] and selected angles [ $^\circ$ ] for  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$ <sup>[a]</sup>.

Sb(1)-F(3)	1.841(4)	F(3)-Sb(1)-F(2)	93.0(2)
Sb(1)-F(4)	1.851(4)	F(2)-Sb(1)-F(1)	171.1(2)
Sb(1)-F(2)	1.861(3)	F(2)-Sb(1)-O(2)#1	86.3(2)
Sb(1)-F(1)	1.870(4)	F(4)-Sb(1)-O(1)	176.4(2)
Sb(1)-O(2)#1	2.003(4)	O(2)#1-Sb(1)-O(1)	86.4(2)
Sb(1)-O(1)	2.004(4)	O(1)-P(1)-F(5)	110.4(2)
P(1)-O(1)	1.493(4)	O(1)-P(1)-O(2)	117.3(2)
P(1)-F(5)	1.497(4)	F(5)-P(1)-O(2)	106.6(2)
P(1)-O(2)	1.499(4)	O(1)-P(1)-F(6)	106.8(2)
P(1)-F(6)	1.502(3)	F(5)-P(1)-F(6)	104.5(2)
		O(2)-P(1)-F(6)	110.6(2)
		P(1)-O(2)-Sb(1)#1	136.8(3)
		P(1)-O(1)-Sb(1)	138.7(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z

[a] further details about the investigation of the crystal structure can be requested from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, E-mail [crysdata@fiz-Karlsruhe.de](mailto:crysdata@fiz-Karlsruhe.de), under number CSD-XXXXXX.

**Table 4.** Comparative bond distances [ $\text{\AA}$ ] and angles [ $^\circ$ ] (in  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$ , $(\text{SbCl}_4\text{O}_2\text{PCl}_2)_2$  and  $(\text{SbCl}_4\text{O}_2\text{PMe}_2)_2$ 

	$(\text{SbF}_4\text{O}_2\text{PF}_2)_2^{[a]}$	$(\text{SbCl}_4\text{O}_2\text{PCl}_2)_2^{[22]}$	$(\text{SbCl}_4\text{O}_2\text{PMe}_2)_2^{[23]}$
Sb-O (av)	2.004(4)	2.06	2.01
Sb-X (X = F or Cl) (av)	1.856(4)	2.30	2.35
P-O (av)	1.496(4)	1.50	1.55
O-Sb-O	86.4(2)	83	87
O-P-O	117.3(2)	116	113

[a] present work

(SbF <sub>4</sub> O <sub>2</sub> PF <sub>2</sub> ) <sub>2</sub>											
Calcd frequencies [cm <sup>-1</sup> ] <sup>[a]</sup>				Obsd frequencies [cm <sup>-1</sup> ] <sup>[b]</sup>				Calcd frequencies [cm <sup>-1</sup> ] <sup>[a]</sup>			
B3LYP Oxygen-bridged								B3LYP Fluorine-bridged			
Raman		IR		Raman		IR		Raman		IR	
		1252	(1297)			1261	(vs)	1507	1509	(289)	v 28 (Au)
1167	[10]dp			1161	[3]			1147			v 1 (Ag)
1158	[4]p										v 2 (Ag)
		1137	(989)			1158	(vs)		1144	(157)	v 29 (Au)
		991	(409)			1046	(s)		744	(174)	v 30 (Au)
985	[4]dp			1048	[7]			742			v 3 (Ag)
907	[16]p			960	[19]				717	(178)	v 4 (Ag)
		899	(72)			952	(s)	715			v 31 (Au)
		724	(181)			708	(vs,br)	705			v 32 (Au)
721	[3]p			710	[5]				702	(124)	v 5 (Ag)
695	[3]dp			509	[2]				652	(16)	v 6 (Ag)
		693	(156)			684	(vs)	651			v 33 (Au)
687	[12]p			691	[39]			506			v 7 (Ag)
		685	(203)			637	(m)		472	(94)	v 34 (Au)
620	[21]p			632	[100]			467			v 8 (Ag)
		619	(1)						463	(881)	v 35 (Au)
		590	(63)					461			v 36 (Au)
582	[0.2]p								454	(0.3)	v 9 (Ag)
491	[2]p								432	(630)	v 10 (Ag)
		481	(95)			488	(s)		403	(27)	v 37 (Au)
470	[2]p							400			v 11 (Ag)
		464	(134)			458	(sh)	356			v 38 (Au)
440	[12]p			461	[11]				347	(9)	v 12 (Ag)
		433	(13)					330			v 39 (Au)
358	[0.4]p			382	[1]			298			v 13 (Ag)
		345	(45)						281	(120)	v 40 (Au)
276	[1]p			270	[26]			253			v 14 (Ag)
		271	(261)						252	(97)	v 41 (Au)
		269	(114)						248	(102)	v 42 (Au)
		258	(44)					246			v 43 (Au)
257	[2]p			253	[1]				245	(267)	v 15 (Ag)
		252	(10)					229			v 44 (Au)
246	[3]dp			240	[2]				222	(5)	v 16 (Ag)
243	[0.5]dp								215	(4)	v 17 (Ag)
		237	(5)						208	(10)	v 45 (Au)
		229	(0.3)					204			v 46 (Au)
217	[3]p			218	[4]			186			v 18 (Ag)
		209	(0.1)						180	(0.3)	v 47 (Au)
207	[1]dp							172			v 19 (Ag)
197	[2]p			196	[2]				166	(19)	v 20 (Ag)
		191	(4)					153			v 48 (Au)
177	[1]p							139			v 21 (Ag)
170	[0.02]p							121			v 22 (Ag)
		146	(1)						118	(0.04)	v 49 (Au)
		142	(0.1)						114	(2)	v 50 (Au)
133	[0.1]dp			151	[2]			111			v 23 (Ag)
108	[1]dp			118	[2]						v 24 (Ag)
		101	(0.01)								v 51 (Au)
52	[0.1]p										v 25 (Ag)
		48	(0.8)								v 52 (Au)
48	[0.02]p										v 26 (Ag)
		46	(0.9)								v 53 (Au)
32	[0.001]p										v 27 (Ag)
		21	(0.7)								v 54 (Au)

[a] IR intensities given in parentheses [km mol<sup>-1</sup>], and Raman intensities given in brackets [A<sup>4</sup>amu<sup>-1</sup>].

[b] Relative IR and Raman intensities given in parentheses and brackets, respectively.

## Figure legends

**Figure 1.** Polynuclear anion  $[\text{PO}_2\text{F}_2 \cdot 2\text{AsF}_5]^-$ .

**Figure 2.** Ortep Plot of  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$ ; thermal ellipsoids are shown at the 30% probability level.

**Figure 3.** Packing diagram of  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$  along the *b*-axis showing the formation of a layered chain polymer through  $\text{P} \cdots \text{F}$  bridges.

**Figure 4.** IR and Raman spectra of  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$ .

**Figure 5.** Formation mechanism of  $(\text{SbF}_4\text{O}_2\text{PF}_2)_2$ .



Figure 1

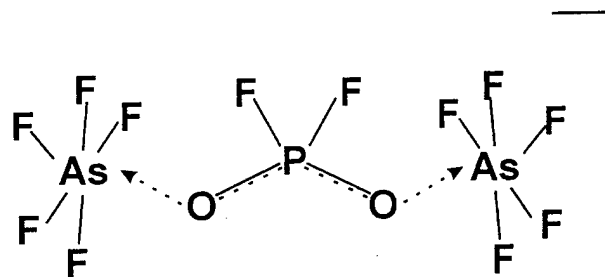


Figure 2

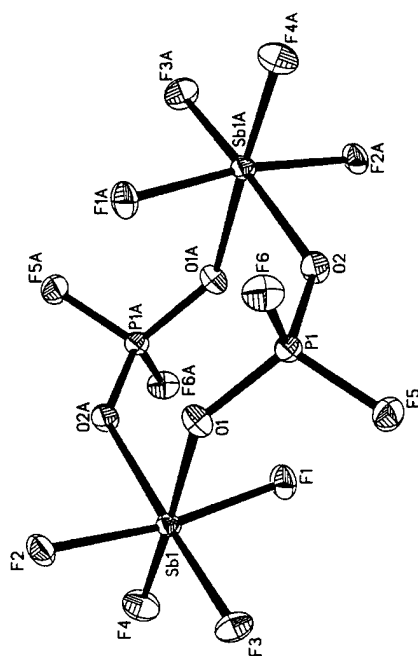


Figure 3

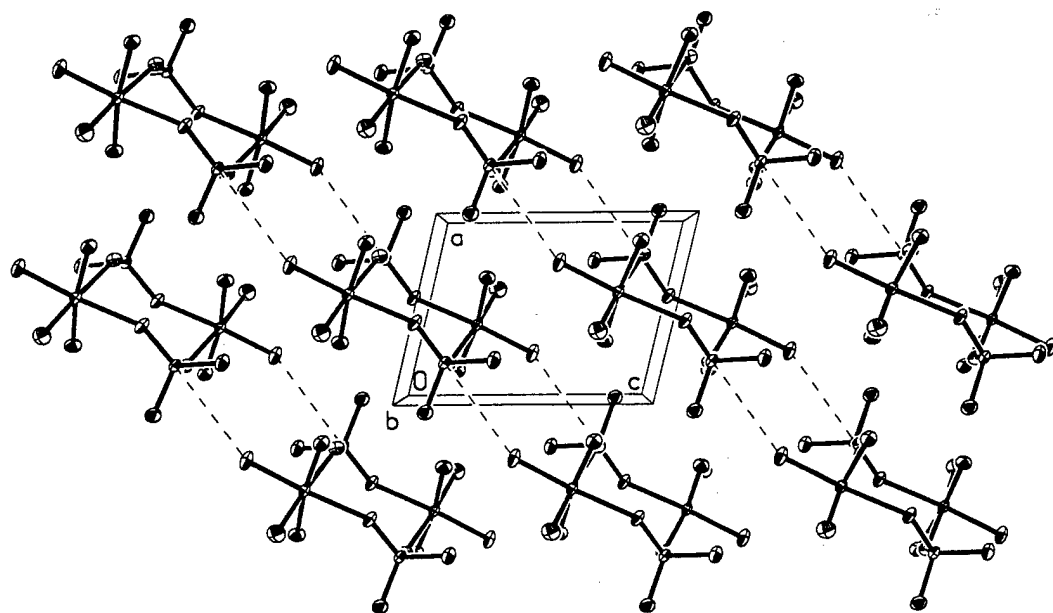


Figure 4

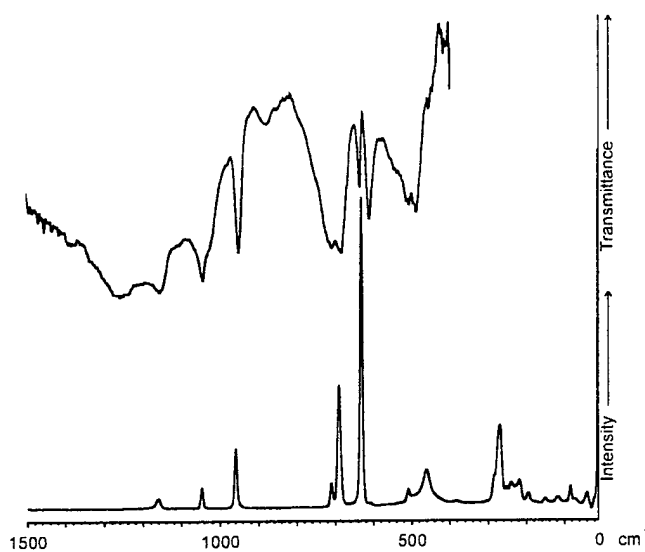


Figure 5

